

Date of Application and filing Complete Specification:
18 Feb., 1966 No. 7366/66.

1,130,540



Complete Specification Published: 16 Oct., 1968.

© Crown Copyright 1968.

Index at Acceptance:—C7 U(4J, 4Q, 5, 7F).

Int. Cl.:—C 23 f 7/24.

COMPLETE SPECIFICATION.

Protecting Silver Against Tarnish.

We, J. GODDARD & SONS LIMITED, of 15/35, Nelson Street, Leicester, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to the protection of clean silver surfaces against tarnish and is particularly but not exclusively concerned with the application of a long term finish to newly mass produced articles before despatch to wholesalers. The current practice is for such articles to be buffed or otherwise hand treated which produces a not entirely satisfactory greasy finish and/or is time consuming and expensive. The invention makes it possible to include the protecting of the finished surface as a step in the production run, with all the consequent advantages from from the point of view of factory lay-out and ergonometrics, and to obtain a finish of high quality which easily lasts the normal shelf life until the article reaches the user.

The process of the invention comprises wetting a clean silver surface of an article with a solution comprising 99 parts by weight of a volatile organic solvent and from 0.1 to 1.8 parts by weight of an organic solute containing an —SH group and capable of forming a transparent colourless protective layer on the silver surface, allowing the solution to react with the surface to form such a layer, allowing the solvent to evaporate, washing the surface with a detergent solution, rinsing the surface with hot water and allowing it to dry.

Silver surfaces suitable for treatment according to the invention include pure silver and silver alloys, such as the generally available sterling and Britannia silver, and plated

[Price

silver surfaces. Impurities do not substantially affect the treatment which may of course be applied to an article only part of which has a silver surface, provided the remainder of the article is protected or inert to the treatment.

The wetting of the silver surface may be carried out by spraying or dipping in a vat. The invention includes both the solution as hereinbefore defined suitable for use in the process of the invention, and the resulting treated articles.

A very wide range of solvents are suitable for use according to the invention. The criteria involved in the selection confronting the chemist making up the solution are mainly rate of evaporation under the intended process conditions, dissolving power for the intended solute, and industrial considerations such as flammability, toxicity, odour, and expense. Glycol ethers generally evaporate too slowly. Simple ethers are flammable and toxic. The lower alcohols are poor solvents and ethyl alcohol is flammable and the essential denaturing agents tend to interfere with the resulting finish. It is not possible to lay down mathematical limits for the physical properties of suitable solvents or to write a general formula. Nor is it suggested that any volatile organic solvent is suitable but a skilled chemist would have no difficulty in choosing a suitable solvent for any particular purpose in the light of this general discussion. Halohydrocarbons have been found most suitable: carbon tetrachloride is relatively toxic; perchloroethylene involves heating the treatment solution in order to provide a satisfactory evaporation rate; methylene dichloride has a high volatility; trichloroethylene is a good solvent; and 1,1,1-

trichloroethane is the best solvent we know. Solvent purity does not appear to be important and commercially available grades such as dry clean trichloroethylene have proved satisfactory.

The solute proportions are important. The said 0.1 parts by weight per 99 parts by weight of solvent has been found to give effective cover but 1 part by weight as aforesaid is preferred. Above 1.8 parts by weight as aforesaid, excess solute is left on the treated surface after the solvent has evaporated. This is wasteful and disadvantageous because most solutes are unpleasant greasy substances which are difficult to remove.

Almost all organic compounds containing an —SH group react with silver surfaces with the formation of —SAg group. If the organic chain is long enough a protective monomolecular layer is formed. Some such layers are opaque and some are coloured but a number of compounds give satisfactory transparent colourless protective layers. The suitability of a particular compound can readily be determined by routine trial. Mercaptans and thioglycollates having at least 12 C atoms in the chain are satisfactory but C12 compounds themselves tend to decompose after a short time and accelerate tarnishing. C16 and C18 compounds are preferred. Up to C24 compounds have been tested and found effective but are not presently available on the market. However we see no reason why compounds up to C30 or even higher should not be useful according to the invention. Stearyl and cetyl mercaptans and thioglycollates are the best substances we know.

The process according to the invention can be carried out on batches of articles contained in baskets or continuously on articles on a conveyor. Either way the articles may be dipped a series of vats or passed through spray booths. Heating the treatment, detergent, and/or rinsing solution facilitates evaporation and/or drying to a smear-free finish. The treatment equipment such as vats, baskets and conveyor should be inert to the treatment solution, detergent, etc. and should not scratch the treated articles. Galvanized iron, aluminium and vitreous enamel are suitable.

The invention is illustrated by the following Examples:

Example 1

1 lb stearyl mercaptan is dissolved in 99 lb dry clean grade trichloroethylene in a galvanized iron tank. Newly manufactured silver plated table forks in a galvanized iron basket are immersed in the solution at room temperature for 2 minutes, drained and dried by evaporation, rinsed in hot detergent solution and in hot water and allowed to dry.

An excellent smear free finish is obtained on 25,000 forks per gallon of treatment solution. 65

Example 2

1 lb cetyl thioglycollate is dissolved in 99 lb 1,1,1-trichloroethane and sprayed at room temperature onto newly manufactured solid Sterling silver spoons in an aluminium spray booth for 2 minutes. The spoons are allowed to drain and dry by evaporation and are then sprayed with a hot detergent solution and with hot water and allowed to dry. The same effect as in Example 1 is achieved. 70 75

WHAT WE CLAIM IS:—

1. A process for protecting a clean silver surface against tarnish which comprises wetting the surface with a solution comprising 99 parts by weight of a volatile organic solvent and from 0.1 to 1.8 parts by weight of an organic solute containing an —SH group and capable of forming a transparent colourless protective layer on the silver surface, allowing the solution to react with the surface to form such a layer, allowing the solvent to evaporate, washing the surface with a detergent solution, rinsing the surface with hot water and allowing it to dry. 80 85

2. A process according to claim 1 in which the wetting is carried out by immersion in a bath. 90

3. A process according to claim 1 in which the wetting is carried out by spraying.

4. A process for protecting a clean silver surface against tarnish substantially as hereinbefore described in either of the Examples. 95

5. A bath solution suitable for use in a process according to any of the preceding claims and comprising 99 parts by weight of a volatile organic solvent and from 0.1 to 1.8 parts by weight of an organic solute containing an —SH group and capable of forming a transparent colourless protective layer on the silver surface. 100 105

6. A bath solution according to claim 5 in which the solvent is a halohydrocarbon.

7. A bath solution according to claim in which the solvent is a trichloroethylene.

8. A bath solution according to claim 6 in which the solvent is 1,1,1-trichloroethane. 110

9. A bath solution according to any of claims 5 to 8 in which the solute is a mercaptan or thioglycollate having at least 12 C atoms in the chain. 115

10. A bath solution according to claim 9 in which the solute is stearyl or cetyl mercaptan or thioglycollate.

11. An article protected by a process according to any of claims 1 to 4. 120

ERIC POTTER & CLARKSON,
Chartered Patent Agents,
For the Applicants,
81 London Road,
Leicester.